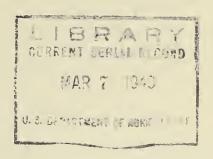
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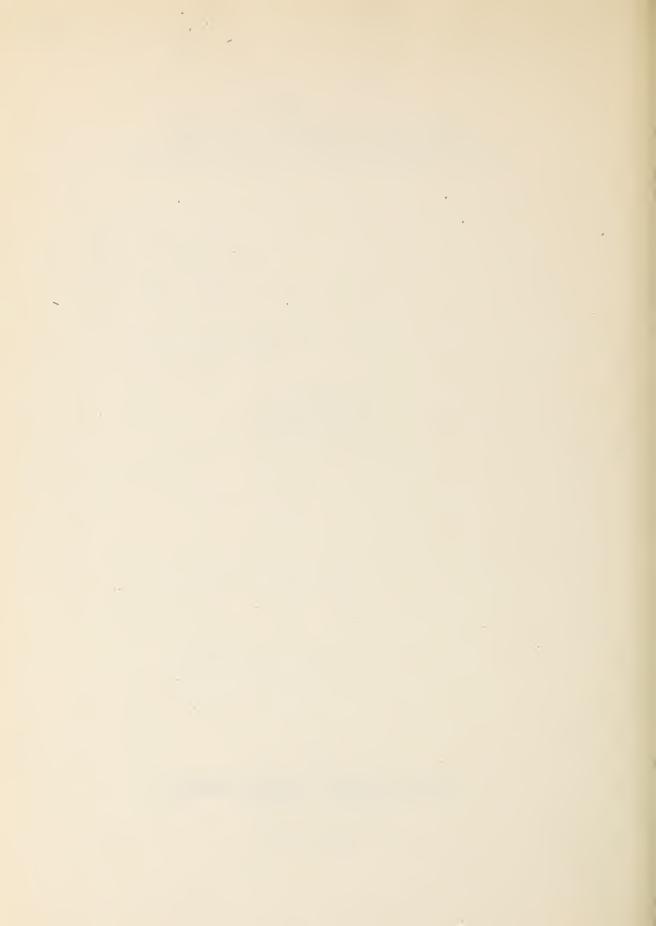
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OIL FROM GRAIN

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## OIL FROM GRAIN1/

Ву

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Grains are distinguished from other items of commerce in the commodity markets by the trade practices followed in their sale, distribution, and utilization. They include wheat, corn, oats, barley, rye, grain sorghums, rice, flaxseed, and soybeans. Botanically, flaxseed and soybeans are not grains, but the procedures followed in their marketing and distribution warrant their being classed as such in the trade. All the grains contain some oil, but only wheat, corn, rice, soybeans, and flaxseed are utilized to produce oils of commerce.

#### COMPOSITION OF OILS

The oils contained in various grains are similar to other vegetable and animal fats and oils in that they are glycerides of long-chain fatty acids, chief of which are palmitic, stearic, oleic, linoleic, and linolenic. Scarcely a generation ago glyceride oil chemistry was little understood and avoided by most chemists as too complicated. Concerted efforts in many of the world's best laboratories, however, have now largely removed the uncertainties surrounding the structure of fats, their chemical composition, the manner in which they are synthesized, and the chemical processes which can be employed to convert them into useful consumer articles. The extent to which each fatty acid is present may now be determined with some accuracy in any fat or oil, and content of the various fatty acids is the criterion most often, but not always, used in determining ultimate use. Characteristics of the five principal acids occurring in the oils under discussion are shown in table 1.

Table	1	Characteristics	of`	common	f'atty	acids

Acids		Number carbon atoms	0	double	0	Molecular weight of triglyceride	Iodine value of triglyceride
Palmitic	0	16		0		807	0
Stearic		18		0		891	0
Oleic	0	18		1		885	86
Linoleic	0	18		2		879	173
Linolenic		18		3		873	262

<sup>1/</sup> This is a revision of paper presented at the 29th Annual Meeting of the American Association of Cereal Chemists, St. Louis, Mo., May 1943, and subsequently published as part of Transactions of the American Association of Cereal Chemists 2(2): 5-19. January 1944.

The structural formula of a typical oil molecule containing one molecule each of oleic, linoleic, and linolenic acids is shown in figure 1.

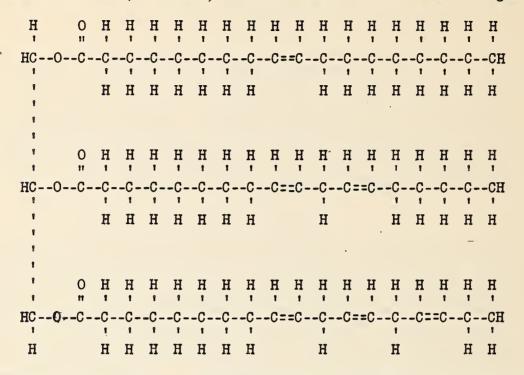


Figure 1. Oleolinoleolinolenin -- a typical glyceride oil molecule

Although it is customary to consider the glyceride in terms of the fatty acids themselves, it constantly must be kept in mind that the oil is actually a mixture of glyceryl esters of the acids, which are combined, three acids per glyceride molecule, in a mixed manner.

The approximate percentages of various fatty acids present in the oils under consideration are shown in table 2. The methods for determining

Table 2.- Approximate fatty acid composition of various oils in terms of glycerides

Oil from	:Fatty acids							
011 11 011	:	Palmitic:	Stearic	: Oleic :	Linoleic:	Linolenic		
		Percent	Percent	Percent	Percent	Percent		
Corn		8	4	45	43	0		
Rice	٥	18	4	48	30	ő		
Soybean	:	10	5	24	56	5		
Linseed	0	8	2	21	21	48		
Wheat germ		14	2	26	52	6		
	0							

these data have been revised so frequently and the variations from sample to sample are so great that the figures should be considered only as illustrative of the general types and amounts of acids present.

In some cases the data represent averages of a number of determinations made at this Laboratory on typical oils, and in others they represent single analyses of typical oils, either from this Laboratory or from the literature. Moreover, several minor acids, such as arachidic, lignoceric, etc., have been included with whichever acid shown they most closely resemble.

In edible products, the palmitic, stearic, and oleic acids are most desired. On the other hand, paints, varnishes, and protective coatings depend upon the drying characteristics of the more unsaturated linoleic and linolenic acids. It should be pointed out in this connection, however, that industry requires tremendous amounts of two other types of fatty acids, namely, short-chain saturated acids and conjugated unsaturated acids, which do not occur to any extent in grain oils. Lauric acid represents the first type and is found chiefly in coconut oil. It is a 12-carbon saturated acid and is valued because of the lathering properties it imparts to soap. The other type is exemplified by eleostearic acid in tung oil. Acids of this latter type are all highly unsaturated, and the distinctive feature is that double bonds are in the conjugated position, rather than nonconjugated as in linolenic and linoleic acids. For instance, eleostearic acid is an 18-carbon atom with 3 double bonds, but the adjacent double bonds are separated by only 2 carbon atoms instead of 3 as in linolenic acid. Oils containing these acids are prized because of the water and alkali resistance of protective coatings made from them.

Considerable attention has been given to the manner in which the various fatty acids in a given oil are distributed to comprise the glycerides. It was once believed that all the acids are present as simple triglycerides, i.e., that all the stearic acid is present as tristearin, all the oleic acid as triolein, etc., but this belief was abandoned long ago. It might be postulated that distribution is perfectly random and, although many fats do appear to have a nearly random distribution, there are frequent examples of oils and fats in which apparently nature has not chosen to combine the several component acids in exactly statistical or random arrangement. The statistical point of view has been explored by Longenecker (2)2/; and the laboratory of Hilditch (1) at the University of Liverpool has made extensive studies of glyceride distributions in a wide variety of fatty materials, employing crystallization procedures for fractionating the various components. The problem is an important one, but the tools which we now have for solving it are hardly adequate. In a recent contribution of Walker and Mills (4), chromatographic absorption is employed in a new approach to the question of glyceride structures in linseed oil.

<sup>2/</sup> Numbers in parentheses refer to literature cited.

Glyceride compositions, if considered casually, might appear hopelessly complex, but this is not the case. In fact, they are quite simple in comparison with many other important naturally occurring products. The most important consideration is the total amount of unsaturation present in a given glyceride molecule. In grain oils containing linolenic acid the most highly unsaturated compound is trilinolenin, containing 9 double bonds, and the opposite extreme is represented by a completely saturated glyceride. Thus, there are but 10 possible compounds distinguishable in terms of total unsaturation. Where linolenic acid is absent, analogous reasoning indicates a maximum of 7 compounds. Obviously, there are several possible ways in which the various acids can be coupled to glycerin to produce some of the molecules. For example, a glyceride having 5 double bonds might conceivably be any of the following:

linolenic	linoleic	linolenic
linoleic	linoleic	oleic
saturated	oleic	oleic

Further variations might be made in each of these arrangements by interchanging the  $\alpha$  and  $\beta$  positions and by substituting palmitic for stearic acid or vice versa. In comparison with crude petroleum oils, coal, and other organic materials, however, the picture presented by naturally occurring glycerides is simple indeed.

In not all cases is it the glyceride material itself that is valued in an oil; frequently the minor constituents of even our major oils are found as important articles of commerce. Wheat germ oil is produced as a source of vitamin E, the tocopherols. The production of phosphatides from crude soybean oil is carried out on a large scale, and the same oil is also a source of stigmasterol and other sterols.

# Processing for Oil

Oilseed crushing is a very old industry and is carried on in various parts of the world by means of the widest variety of equipment. In out-of-the-way places primitive methods are still used. Such crude devices as presses powered by driven wedges are not uncommon, for example, in remote sections of China and Manchuria. In the United States and Europe, oilseed processing is rather highly mechanized, however, and in many instances particular industries are concentrated in a few extremely large mills.

In the United States, oils are removed from grains by three processes, namely, hydraulic pressing, continuous pressing in screw presses, and solvent extraction. All three are widely used. The hydraulic press is the result of evolutionary changes in the ancient wedge-operated press, and its operation is a batch performance. Hydraulic presses still constitute most of our installed oilseed processing facilities, but the

advantages of continuous operation have greatly encouraged adoption of screw presses and the continuous type of solvent extractors for handling materials suitable for processing in such equipment.

Hydraulic presses .- There are three types of hydraulic presses used to crush oilseeds in this country, namely, box, plate, and cage presses. In all three, a charge of prepared oilseeds is compressed by the upward thrust of a hydraulic ram. Box and plate presses are quite similar, each consisting of a massive head plate supported by four sturdy posts at the corners, a movable bottom or floor plate, and a number of plates or boxes hanging one below the other from the head plate to divide the press into horizontal compartments. In plate presses, the compartments are separated by approximately 24 flat steel plates, while in box presses each compartment is a steel box formed by overlapping projections from the top and bottom sides of successive plates. Figure 2 shows a typical box-type of press. It is generally used in the cottonseed industry, but other cilseeds are frequently crushed with such presses, particularly soybeans. The oil-bearing material is rolled into thin flakes, cooked in a special cooker, and then molded into firm cakes which are wrapped with hair cloths and inserted in the press boxes. Approximately 15 cakes are placed in each press, one in each of the boxes.

Plate presses are widely used on linseed. The rolled and cooked seed is packed into rectangular cakes and wrapped in hair cloths, much the same as with cottonseed. The cakes are then inserted between the press plates, and on each plate there are usually either special corrugations or a thick mat of rope or similar material to ease the drainage of oil.

A compression or drainage period of 15 to 30 minutes for soybeans, and approximately an hour for linseed, is allowed for oil to flow out of the hot meal, and it is collected at the base of the press in a trough from which it drains or is pumped to the oil tanks. The cakes are removed from the press, the cloths are removed, the edges are trimmed from the slabs and returned for repressing, and the cakes subsequently are ground for incorporation in mixed feeds.

In plate and box presses, pressures within the compressed meal are usually somewhat less than 2,000 pounds per square inch, but some oilseeds require considerably higher pressures. This is particularly true in pressing castor beans, and cage presses are the rule for this operation. They are also used to some extent on both linseed and soybeans. As the name implies, instead of plates, boxes, and press cloths, the cage press employs a square or cylindrical cage constructed of closely spaced longitudinal steel bars. A ram is forced upward through the cage, compressing the prepared oilseeds which have been charged through the top and retained by locking a heavy press head over the top of the cage. The oil is forced out between the cage bars, and after drainage has ceased, the press head is removed to permit discharge of the meal by further raising of the ram.

Continuous screw presses. - Hydraulic presses require much hand labor and have other disadvantages inherent in processes that are not amenable to continuous flow operation. Many oilseeds can be crushed in continuous presses, however, and most of the oil-producing grains are examples. The presses are built like a large-scale meat grinder, with a powerful rotating screw continuously forcing cooked oilseeds through an expression chamber under tremendous pressure. The expression chamber is a cylindrical cage composed of closely placed steel bars between which the oil escapes.

Continuous presses are used the world over and are manufactured in many countries. American machines, however, are much more highly perfected. Only two makes are manufactured in large quantities in this country, the Anderson Expeller and the French screw press. These machines, each having a capacity of approximately 25 tons per day, are installed either singly or in batteries consisting of as many as several dozen units. A close-up view of the French screw press is shown in figure 3, and an inside view of a soybean mill containing more than 40 Anderson Expellers is shown in figure 4.

Continuous screw presses now are used much more widely than any other type of equipment in the grain oil industries. Their success in the soybean processing field has been outstanding, and they are particularly suited for installing in small mills serving a limited area. Their principal disadvantage, especially during the current fat shortage, is that they do not remove all the oil. They are somewhat better than hydraulic presses in this respect, but even under exceptionally favorable conditions the oil content of the residual press cake is seldom less than 4 percent. Good solvent extraction practice, on the other hand, reduces oil in the meal to less than 1 percent.

Solvent extraction. The use of volatile fat solvents to extract oil from oilseeds is an old practice, but it has been thoroughly modernized during the interval between World Wars I and II. Earlier methods were entirely batch operations in which prepared seeds were charged into either stationary or rotating extraction kettles, leached with solvent, dried, and discharged. The solvent was recovered from the oil by distillation. Many of these extractors are still in use, some on a very large scale.

Following the first World War, Germany developed a considerable industry in the processing of imported Manchurian soybeans. Tremendous mills were built, and a number of continuous extraction systems were developed in which soybean flakes are countercurrently washed with a continuous stream of oil solvent. Success of these systems has resulted in their adoption in many other parts of the world, including the United States. The first preliminary operations of one of these extractors date back to 1924 in this country, but it was not until 10 years later that permanent installations were made. During the 1930's a considerable number of German continuous-extraction plants were built in the United States, and simultaneously American manufacturers undertook development of similar processes. Now approximately 10 leading process-equipment firms are building continuous-extraction systems in this country.

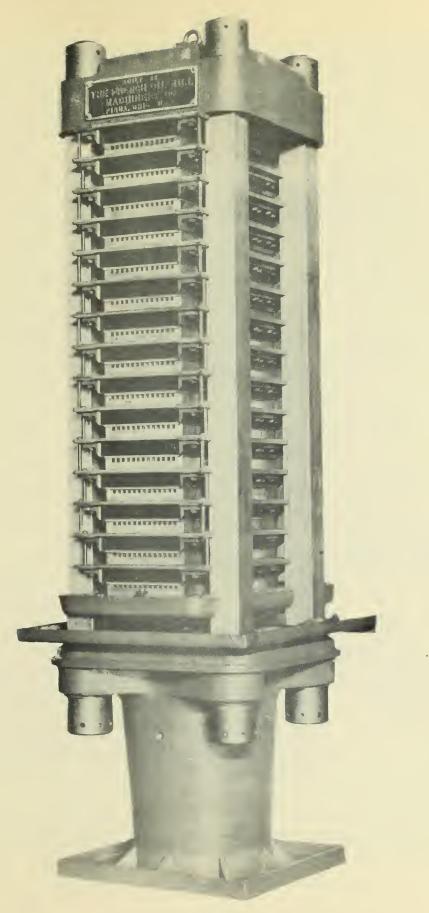
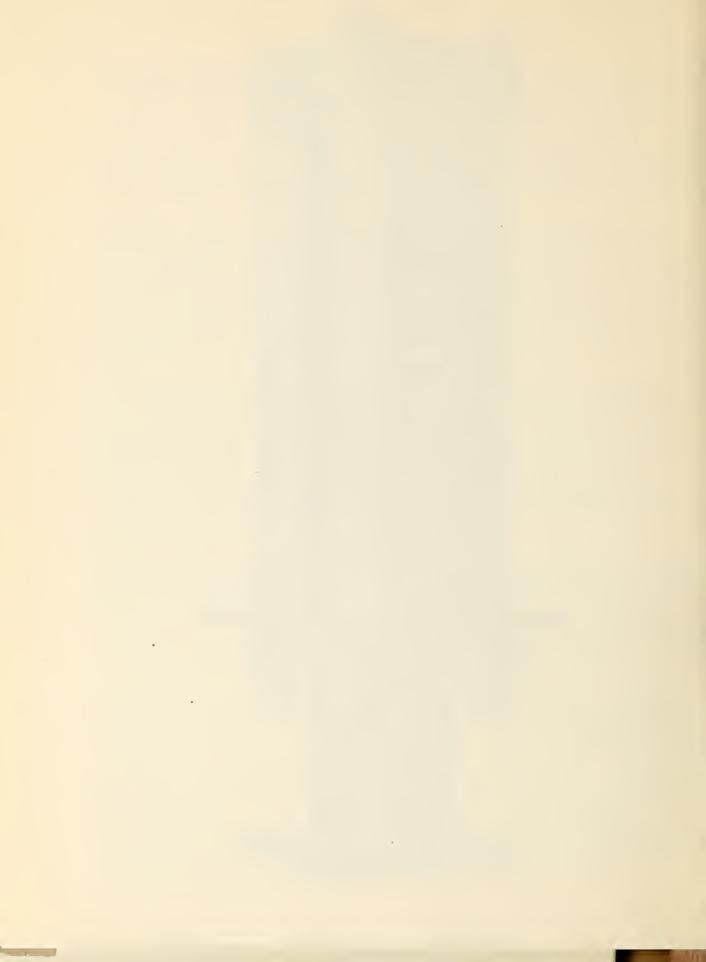
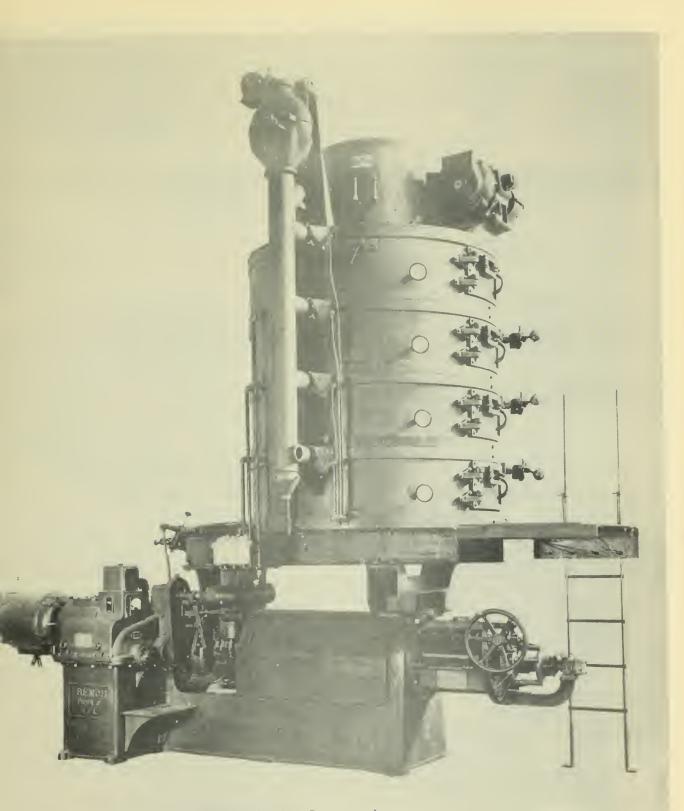


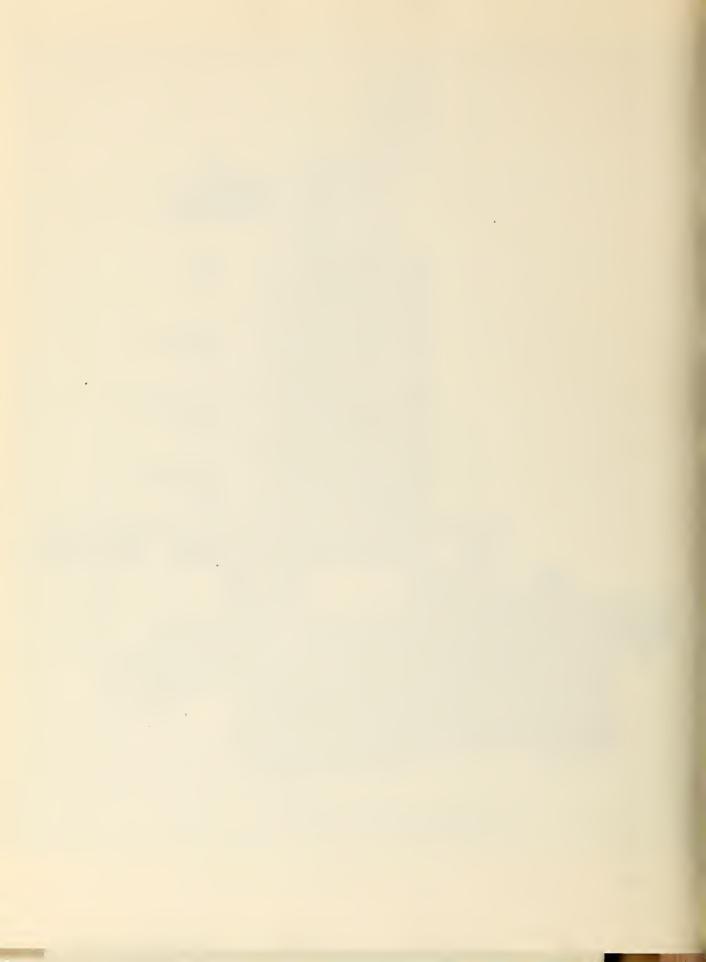
FIGURE 2 .- - Box type of hydraulic press. (Courtesy French Oil Mill Machinery Company)





Four-High Cooker Dryer and
Four Section Mechanical Screw Press

FIGURE 3. -- The French screw press. (Courtesy French Oil Mill Machinery Company)



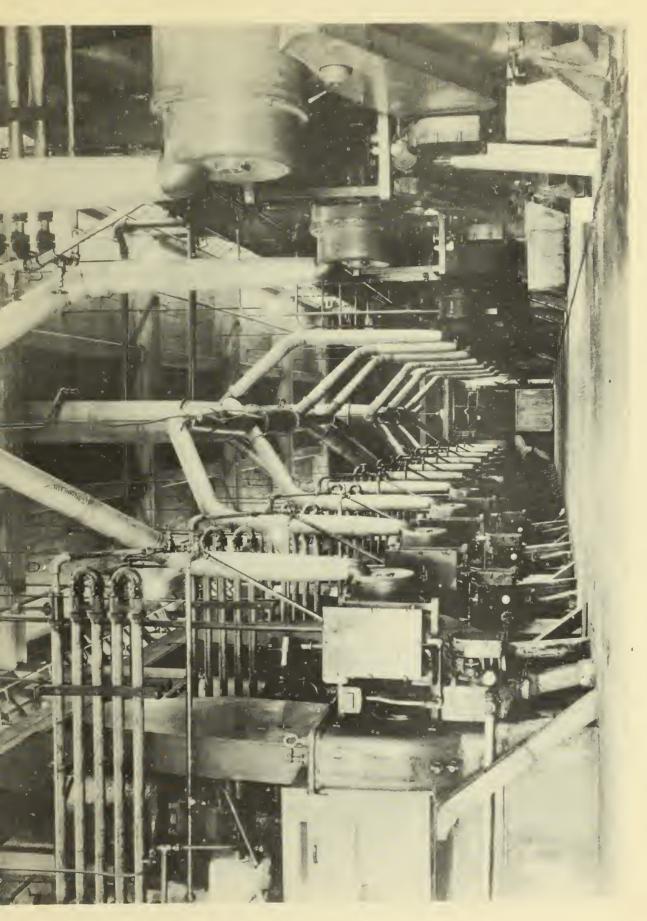
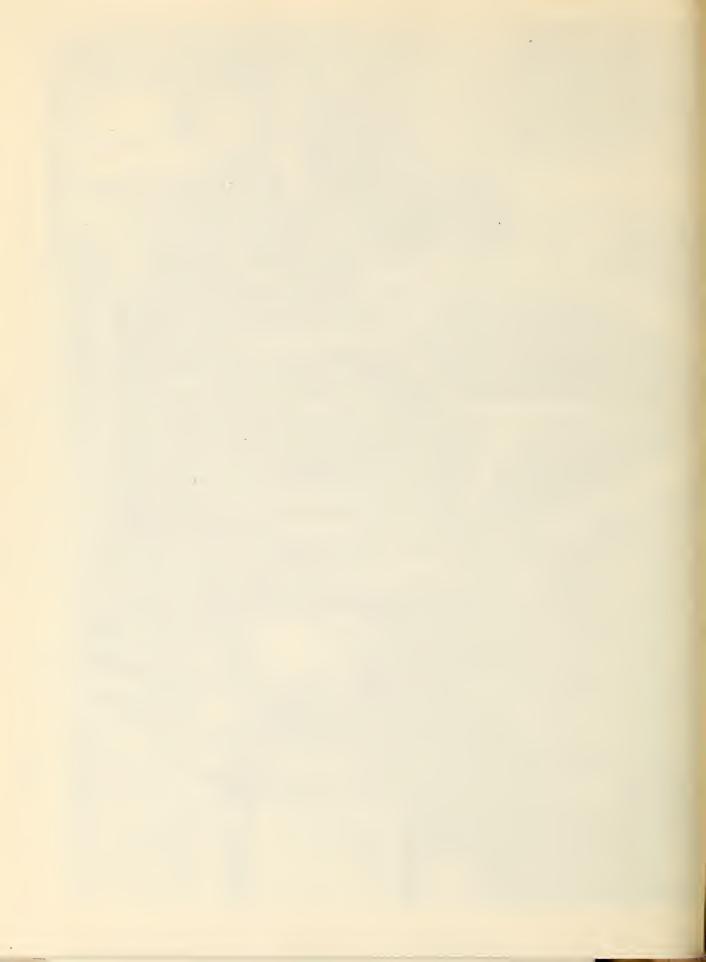


FIGURE 4. -- Interior of soybean mill operating more than 40 Anderson Expellers.

(Courtesy V. D. Anderson Company)



Briefly, the steps in continuous extraction comprise grinding, flaking, extraction, separation of solvent from oil, and separation of solvent from meal. The oilseeds are first rolled into thin flakes to reduce the amount of diffusion required for the oil to escape. They are conveyed then through a continuous-contacting device in which they are washed countercurrently with a solvent. The apparatus for this step is distinctively different in each process and consists of such arrangements as screw conveyors, drag link conveyors, bucket elevators, etc., specially designed for the task. The solvent is evaporated from both the oil and the spent meal, condensed, and used over again. The oilsolvent solution known as miscella, is concentrated in pre-evaporators, and final traces of solvent are removed by scrubbing countercurrently with steam. In the case of the spent meal, steam-jacketed screw conveyors are generally used to drive off the absorbed solvent.

The contacting device of one typical system is shown diagrammatically in figure 5. A pair of conveyor chains encircle upper and lower sprocket wheels and have attached a large number of sieve-bottom baskets containing oilseed flakes. The flakes are introduced into the top basket on the descending side and are discharged by inverting each basket at the top, after it has completed one circuit. The ascending baskets are washed with a spray of fresh solvent which trickles downward countercurrently. The "half miscella" collected from this side is then re-used to wash the descending chain of baskets. The resulting "full miscella" is pumped to distillation equipment, and the spent meal is conveyed through a series of driers.

## Grain Oils Produced by All Three Processes

According to the Bureau of the Census, the number of mills engaged in the processing of soybeans during the calendar year 1946 was 276; of corn germ, 27; and of linseed, 44. As previously stated, all three processing methods are used to produce grain oils. The extent to which each method is used varies widely.

Soybeans. - Soybeans are more easily processed for oil than linseed or cereal grains. The approximately 18 percent of oil in the whole bean is contained mainly in the cotyledons which comprise fully 90 percent of the seed and contain 20 to 21 percent oil. The germ constitutes only 2 percent of the seed and contains approximately 10 percent oil. The remaining 8 percent is the hull which contains only 0.6 percent oil. The germ and hull are so small a proportion of the whole bean that they are not separated ordinarily in the milling process. In the production of soy flour, however, the hulls are separated.

Soybeans are processed principally in screw presses, and to a small extent in hydraulic equipment. For many years there has been a gradual increase in the proportion processed in solvent mills and a corresponding decline in the proportion crushed in hydraulic presses. The actual figures are shown in table 3. To meet the impending shortage of fats

and feeds, however, soybean production during World War II was doubled over that of the years immediately preceding, and quantities of beans were made available for crushing far in excess of the normal crushing capacity. It was necessary, therefore, to ship large quantities of scybeans to southern cottonseed mills and to linseed and copra mills located in the East and on the Pacific coast. For this reason, the relative proportion of hydraulic soybean crushing increased during 1942 and 1943.

Table 3.- Comparison of three common processing methods used on soybeans in recent years

Crop year,	Percentage proce	: Total amount,		
to October			: Hydraulic	: processed=/
to october	screw press :	extraction	: press	
1941 1942 1943 1944 1945 1946	74.1 63.2 65.2 70.5 64.2 63.9	24.1 16.3 16.4 20.0 28.2 26.6	1.8 20.5 18.4 9.5 7.6 9.5	77.1 133.4 142.3 153.4 159.4 170.2

 $\frac{1}{\sqrt{1000}}$  Millions of bushels.

Data compiled by Bureau of the Census and the Northern Regional Research Laboratory.

Linseed. The soybean industry has undergone tremendous development in recent years, and the technological advances that have made possible the installation of so much modern oilseed-processing equipment have created repercussions throughout the fats and oils industries. Within the past 2 or 3 years, for example, a large part of the linseed-crushing industry has replaced hydraulic presses with continuous screw presses. The change had been contemplated for many years but was delayed considerably by lack of a suitable cooking process. Some mills now crush both soybeans and linseed in the same continuous presses, since only minor changes are necessary to adapt the machine to either oilseed.

Linseed contains approximately 39 percent oil and must be flaked or ground and properly tempered under accurately controlled moisture conditions before expression in order to obtain a high yield. Some seed is processed without cooking, however, to produce "cold-pressed" oil which has a milder and less bitter taste than the hot-pressed product. Solvent extraction, both batch and continuous, has been used to a limited extent, and the introduction of continuous solvent extraction in the linseed industry on a large scale now appears imminent.

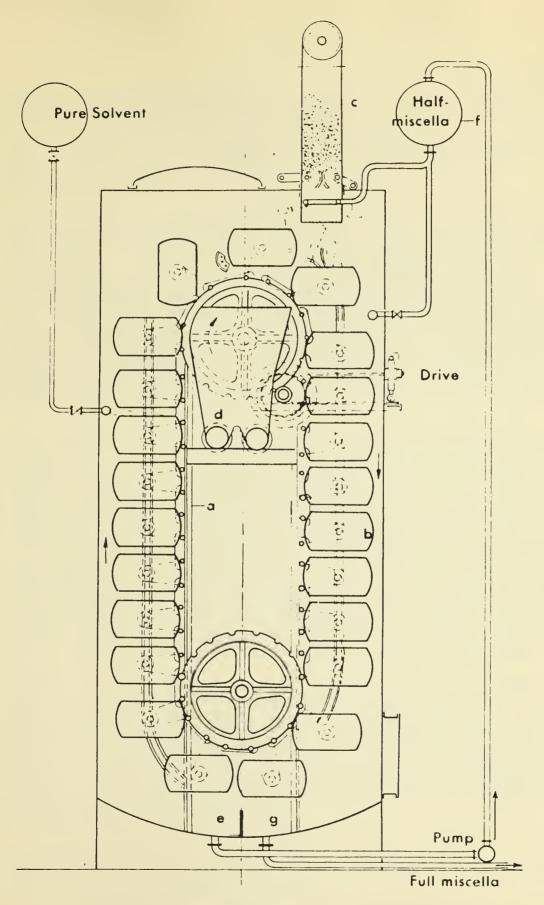


FIGURE 5.-- A typical solvent extractor.



Corn germ. - Corn oil is a byproduct of both the wet and dry corn-milling industries and is obtained from the germ which is removed either mechanically or by floating on the resultant slurry of starch and water after the steeped grain has been ground. Yellow corn contains approximately 5 percent oil, on a dry basis, but the germ is approximately 35 percent oil, which represents two-thirds or more of the total oil present in the kernel.

Germ from wet-milling process is fairly pure and after the dissolving of water-soluble constituents which are removed in the degerminating operations, contains 50 percent oil. It is dried, ground, and pressed in screw presses. In some mills the pressing is a comparatively light one, leaving 13 to 15 percent oil in the meal, and the press cake is then solvent extracted. Both batch and continuous extractors are in use. In dry milling the germ separation is less efficient, and the product contains only 20 percent oil, more or less, depending on various processing practices. Not all this germ is processed for oil, but a certain amount is pressed in screw presses. A typical oil yield by wet milling is 1.64 pounds per bushel, and in dry milling one-half pound per bushel is considered average. Some corn oil has been produced, too, by the solvent extraction of distillers' grains.

Wheat germ. Wheat contains approximately 2 percent oil, which is distributed in all parts of the grain-bran, starch, and germ. The germ contains 12 to 16 percent oil but constitutes only 2 to 3 percent of the weight of the kernel. On the average, only one-eighth of the total oil is found in the germ, and only one-tenth of the germ is recovered in the degermination step of flour milling, so the over-all yield of oil is extremely low. About one-fourth of the total oil is in the bran, and the balance is in the starch portion. Two processes are used to recover wheat germ oil--cold pressing and solvent extraction. Pressing is accomplished in screw presses, and only half the oil is removed. Batch solvent extraction is also employed by which higher yields can be obtained. In both instances considerable care is necessary to avoid heating and consequent destruction of the vitamin E, or tocopherols, which are contained in the 3.5 to 4 percent of unsaponifiable matter.

Rice bran. - Rice oil is produced mainly in Japan and is not a common commodity in this country. However, there is a small domestic production. The average yield of bran in rice polishing is 17 percent. It consists of the cuticle and embryo plus a small amount of hull and is extremely rich in vitamin B-complex. If the hulls are substantially absent, it is known as rice meal. Typical rice bran contains 14 to 15 percent oil, and, although Japanese rice oil is obtained by hydraulic pressing, it is reported that the only American production in recent years has been by solvent extraction.

#### Uses

The relative proportions in which the three leading grain oils are used in various channels are shown in table 4.

Table 4.- Consumption of grain oils for specified purposes, 1946

Fields of use	Oil				
	Soybean:	Linseed:	Corn		
Factory consumption, million pounds Foods, percent Soap, percent Drying oil industries, percent Miscellaneous fields, including loss, percent	1,081 92 1/ 3	539 0 <u>1</u> / 85	18 81 2 <u>1</u> /		
7/9					

1/ Less than 0.5 percent.

Each oil has characteristics which render it particularly well suited for specific purposes. The only one that enjoys any considerable diversity of consumption is soybean oil and even it is predominantly an edible oil. Its properties are intermediate between those of food oils and drying oils, and it exhibits, therefore, considerable promise as raw material for development of new industrial products. This subject will be discussed subsequently.

More than half of the soybean oil consumption is in shortenings, for which purpose it is alkali-refined, bleached, hydrogenated, deodorized, and compounded or emulsified with air or other gas. About one-sixth is used in oleomargarine, and a substantial quantity is used also in salad and cooking oils. Because it is primarily an edible oil, its price follows that of lard and cottonseed oil, and it is marketed through the same channels.

Linseed oil, of course, is a drying oil and is consumed mainly in paints, varnishes, lincleum, printing ink, and similar compositions. Its use in soap is negligible--less than 1 percent of the total amount consumed. In European and Asiatic countries, particularly in Russia, cold-pressed linseed oil is an edible product. Considerable American linseed oil was shipped abroad during the recent war for food uses, and shortenings containing linseed oil have been used quite widely in Canada.

Corn oil is an edible oil. More specifically, it is a salad oil and is not used in shortening or oleomargarine to any great extent. The crude oil is ordinarily refined, bleached, deodorized, and winterized.

The low yields of wheat germ oil and the care required in producing it have prevented its becoming an important oil in industry. Its only use is as a source of vitamin E in pharmaceuticals for human and livestock use. The lack of suitable assay methods has created difficulties in development of a market. Its price in 1948 was approximately \$1.70 per pound.

Rice oil is subject to rapid deterioration, apparently caused by enzymatic hydrolysis, and, consequently, it is used almost entirely in soap.

## Outlook for Expanded Usage in Other Fields

The paint or coatings industry is the third largest single user of fats and oils and is constantly developing new applications for them. The full value of fats and oils as raw materials for the manufacture of new compositions such as resins, coatings, artificial rubber, and other polymeric products, however, has not been generally appreciated, but development of this field through research is now underway along several lines of attack.

Fractionation.- For many applications, it is found that the naturally occurring oils are not ideally suited because of preponderance or insufficiency of certain constituent acids. For such cases, fractionation processes have been developed for separating the components desired from those which are not essential. In most cases both fractions can be used to better advantage than the original oil. Some fractionation processes are applied directly to the oils, as glycerides, and the degree of fractionation attainable in such instances is obviously limited by the mixed condition in which the fatty acids are combined. In other methods the limitations imposed by mixed constitution are overcome by splitting the oils into free acids and glycerine, fractionating the acids themselves, and reconstituting glycerides or similar polyhydric esters.

Several tools are available for fractionating fatty materials, the oldest of which, from a commercial standpoint, is crystallization. The present practice is to chill the oil or a solution of the oil in a solvent in order to crystallize out the more saturated and, in some cases, the components of greater chain length. The phases are separated by settling and decanting the supernatant liquor, by filtration, or by centrifuging. An example of this process, conducted on a large scale, is the winterizing of soybean, cottonseed, corn, and other oils to remove those constituents which might crystallize out of salad oils during storage and produce an unwelcome turbidity. Similar processes are conducted on vegetable oil fatty acids to obtain fractions rich in linoleic acid for alkyd-type resins or for producing technically pure oleic and stearic acids.

Another fractionating tool, widely used in many industries, is fractional distillation or rectification. Glyceride oils themselves will not distill in ordinary rectifying equipment, but the free fatty acids can be readily fractionated under high vacuum. The process is conducted on a large scale by several firms, the principal materials so treated being soybean and fish oils. Separation by distillation is dependent mainly upon chain length, the shorter acids distilling more readily. With soybean acids the primary objective is separation of the palmitic acid, leaving the C1g acids as a residue. The resulting still bottoms then can be re-esterified with glycerine to yield an oil which, having been depleted of its palmitic acid, is considerably more unsaturated than the original oil and, consequently, a better drying oil. The residue is

used also in preparing alkyd resins. Although fractional distillation effects a separation mainly by virtue of differences in chain length, it is possible to bring about some separation on the basis of unsaturation, too. The utility of distillation as a tool for modifying oils is limited by the extreme corrosiveness of the free acids and by the expense involved in splitting the oil and reconstituting the glycerides.

Liquid-liquid extraction is now entering the glyceride oil fractionation field. It is an extremely versatile tool, suitable for fractionating either on the basis of chain length or on the basis of unsaturation. Its commercial use in the vegetable oil industry is still in an early stage, but it undoubtedly will be a most important factor in postwar developments. By extraction with furfural, for example, soybean oil can be separated into a fast-drying and an edible fraction, both being far superior to the original oil for the respective uses. Linseed oil can be similarly separated to produce a super-drying extract. A still more important application of liquid-liquid extraction, however, appears to be the preparation of pure fatty acids and their derivatives. Through development of fractionating tools, new quantities of these materials will be made available soon for research workers to use as "building blocks," and their value for the manufacture of the widest variety of industrial materials probably will become much more apparent. Some examples will be given later.

Molecular distillation also has received much attention in the glyceride oil field, and it is conducted on a rather large scale as a specialty manufacturing process. Because of the large molecular size of these glycerides, the distance between the distilling and condensing surfaces must be extremely short, and the vacuum must be so high that this distance is shorter than the mean free path of the molecules being distilled. The molecular or short-path still finds its principal application, at present, in the removal of the unsaponifiable or vitamin-containing portions of oils.

These are not all the tools available for fractionating and modifying oils. Selective adsorption has been employed on a small scale. In some cases it has been found that, when a particular fatty acid composition is desired, two oils can be mixed to achieve the proper average proportions of acids, and the mixture then subjected to catalytic ester-ester interchange to effect the necessary mixed glyceride composition.

## Synthetic Materials Derived from Fatty Acids

The uniformity with which nature synthesizes vast quantities of the five acids listed in table 1 affords industry a valuable source of industrial raw material for the manufacture of synthetic products. The list of such synthetics already in production is much too long, however, to permit mentioning more than a very few.

To visualize the relative proportions of these long-chain acids that are potentially available, the supply must be considered not in terms of the amounts of various oils produced but, instead, in terms of the amounts of fatty acids contained therein. Figure 6 shows graphically the amounts of palmitic, stearic, oleic, linoleic, and linolenic acids which comprised the 1946 production of the three principal "grain" oils in this country. The relative proportion that each oil contributes to the total supply of each individual acid also is indicated. As previously pointed out, each acid has its particular field of utility as determined by its chain length, number of double bonds, and similar characteristics. The most abundant acid in these oils is linoleic which is of great interest because of the pair of unconjugated double bonds which it contains. The three double bonds of linolenic acid lend particular value to it, also, for the preparation of such polymeric products as coatings, resins, etc. It is significant that linseed oil is by far our most abundant source of linolenic acid and that soybean oil is the leading supplier of linoleic acid.

Tung oil substitutes.— Although linseed oil is our principal drying oil from a quantity standpoint, tung oil is much more important strategically. It is vital to the production of water-resistant coatings and owes its superior properties to the fact that the double bonds in eleostearic acid, its main component, are in conjugated rather than in nonconjugated positions. Tung oil comes principally from China and has been very scarce in recent years. The necessity of finding substitutes has fostered a number of recent developments, all of which are based on rearranging double bonds from nonconjugated to conjugated positions. The essential raw materials are the linolenic and linoleic acids in linseed and soybean oils. These tung-oil substitutes are being produced commercially, isomerization of the acids being effected by high-temperature alkali treatment.

Fatty acid amines. - Another field for industrial utilization of fatty acids has been opened by the introduction of a number of fatty acid nitrogen derivatives (3). Removal of a molecule of water from a fatty-acid ammonium soap yields the amide, which can be dehydrated to a nitrile. The nitrile, in turn, can be hydrogenated to yield a fatty-acid amine. This interesting series of compounds is in commercial production, and among the many uses being found for them are waterproofing agents, protective coatings, flotation agents, plasticizers, insect repellents, and textile finishes. Of even greater importance is their potential use as intermediates in the production of new materials not yet available to industry.

Rubber substitutes. - One of the most striking examples of the manner in which fatty products can be synthesized into valuable industrial materials is the rubber substitute, Norepol. It was developed by the Northern Regional Research Laboratory, and its production was undertaken by a number of manufacturers during the rubber emergency of

1942-43. Another material, Norelac, is being manufactured for coating papers to impart moisture resistance and other desirable properties.

Norepol and Norelac, both made from linoleic acid, are only two illustrations of the possibilities for constructing useful molecules from this simple fatty acid. The acid is subjected to controlled polymerization to produce a dicarboxylic acid having a uniform chain length. These undergo reactions with dihydric alcohols and diamines to produce linear polymers of high molecular weight. The products have remarkable properties, as exemplified by Norepol and Norelac, which are the first of a long list of important products heretofore unheard of that may soon be made from these fatty acids which nature obligingly fashions into such useful forms.

### Summary

The important grain oils are corn, soybean, and linseed. Rice bran and wheat germ oils are produced only in small quantities. All of these oils are characterized by their relative contents of five important fatty acids--palmitic, stearic, oleic, linoleic, and linolenic. They are produced by hydraulic pressing, by continuous pressing in screw presses, or by solvent extraction. Recent developments tending to influence their industrial utilization include new methods of fractionation and new synthetic products derived from the fatty acids. Outstanding examples of the latter are a rubber substitute, Norepol, and a resin, Norelac, which are made from linoleic acid. Although their discovery has proved of great value, these are only the first of many similar developments which the future holds for the grain oil industries.

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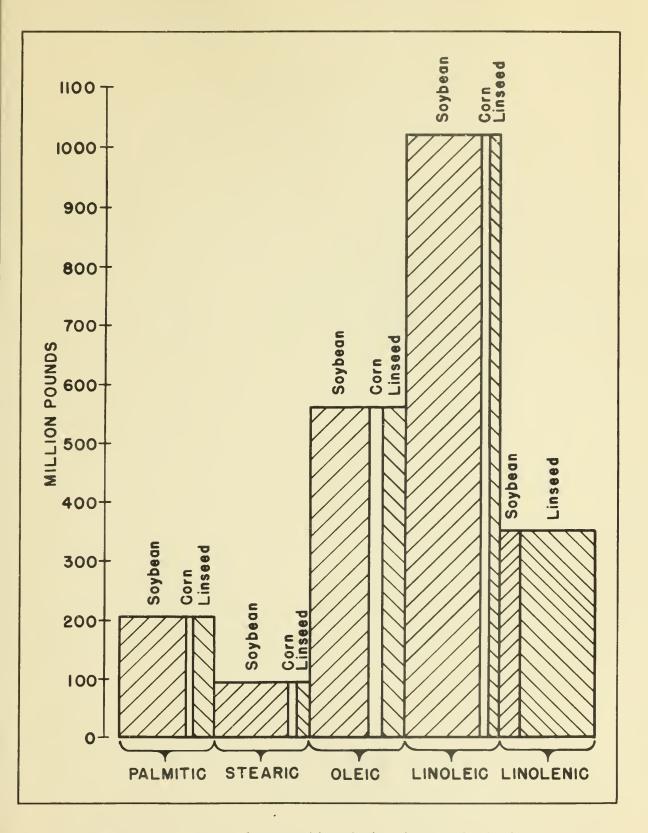


FIGURE 6.--Component fatty acids of the three principal oils produced in 1946.





